

# On the power spectrum of undulations of simulated bilayers.

by

J. Stecki

Department III, Institute of Physical Chemistry,  
Polish Academy of Sciences,  
ul. Kasprzaka 44/52, 01-224 Warszawa, Poland  
March 8, 2013

Abstract.

The best finite Fourier Series for a smooth surface  $h(x, y)$  closest to the positions of heads of amphiphiles in the least-square sense, agrees fully with the Fourier coefficients obtained by a direct summation over raw data points. Both methods produce structure factors  $S(q)$  containing all necessary features: small- $q$  divergence, a minimum, the raise to the ubiquitous nearest neighbor peak near  $q = 2\pi/(\text{coll.diameter})$  and further peaks. The Laurent series is also discussed.

The power spectrum of fluctuations *vel* structure factor  $S(q)$  quantifies the undulations of a simulated bilayer. The deviations from planarity, of either monolayer or bilayer as a whole, are described in terms of an imagined surface  $h(x, y)$  represented as a finite Fourier series  $h(x, y) = \sum \tilde{h}(\mathbf{q}) \exp[i\mathbf{q}\mathbf{R}]$ . The power spectrum is then  $S = \langle \tilde{h}\tilde{h}^* \rangle$  at any given  $q$ . At  $x = |q^2| \rightarrow 0^+$  the theory[1-4] predicts  $1/S = kx^2 + gx$  asymptotically, where  $k$  is the bending (or rigidity) coefficient[1] and  $g$  is the fluctuation lateral tension - slightly larger than the lateral tension  $\Gamma$  determined from pressures[5].

The first point of this Letter is that the size of the region of  $x$  where the asymptotic form is valid, can be estimated quantitatively by plotting the inverse  $1/S$ , further divided by  $x$ , as seen in Figure 14 in Reference[3]. It is extremely small[6,7], but as the quoted Figure[3] and many other such plots show, there is such a small range, it exists[8]. A representation of  $S(x)$  beyond that minuscule asymptotic region would be very useful[6]. Because of the disparity of  $g$  and  $\Gamma$  and for a variety of other reasons,

almost all simulations choose the tensionless state ; there  $S \sim 1/kx^2$ [6,9-16]. Then, as already noted when the  $q^{-4}$  dependence was uncovered[12] for the first time, an expansion in powers of  $1/x$  works suprisingly well. I submit it is most understandable;  $S$  originally had two poles  $x_1 = 0, x_2 = -g/k$  (  $x_2$  produces a new asymptote for  $S$  in the floppy state where  $g < 0$ [17,18]) merging into a double pole at  $g = 0$ . Then  $x^2S$  admits a Taylor expansion  $x^2S = a_{-2} + a_{-1}x + a_0x^2 + a_1x^3 + \dots$  and the Laurent series is  $S = a_{-2}/x^2 + a_{-1}/x + a_0 + a_1x + a_2x^2 + \dots$ . A preliminary fit of finite Laurent series is given in Supplementary Material, making it clear that such representation is feasible[19]. The second point of this Note is then an extension of the original observation that power series of  $x$  works very well but (1) there is no reason whatsoever to stop at two terms and (2)  $a_n$  beyond  $a_{-2}$  need not have direct meaning as proposed[6][8][12].

A most important feature of  $S$  is the appearance of the nearest-neighbor (n.-n.) peak near  $q = 2\pi/\sigma$  ( $\sigma$  being the collision diameter). *This is a must as the bilayer is a liquid.* It seems most obvious that any interpretation of the  $S(q)$  of the bilayer must include some bulk contribution of the liquid type. The structure factors and the radial distribution functions  $g(r)$  of bulk liquids are well known;  $S_{bulk}$  raises from  $S(0)$  (related to compressibility) to the n.-n. peak. To that region of rising  $S$  belongs all the liquid structure contained in  $g(r)$ . Correspondingly,  $S$  of a bilayer raises[17][9,10] above the asymptotic decay to *go through a minimum* and to raise to the n.-n. peak. First such peak was shown some time ago[17] and in a recent work[9,10] several further peaks at still higher values of  $q$  were obtained. It follows that any method which fails to show the minimum in  $S(q)$  (and the n.-n. peak if the  $q$ -range includes  $2\pi/\sigma$ ), is therefore not to be trusted.

This caveat applies to methods based on gridding, which have never shown the ubiquitous nearest-neighbor peak.

The structure of any liquid is described statistically as the density-density correlation function  $\langle \delta\rho(1)\delta\rho(2) \rangle$ , also for inhomogeneous fluids and for interfaces[20-22]. In our case of a nearly flat bilayer with periodic boundary conditions, it reduces to a function of  $z_1, z_2, \mathbf{R}_{12}$  and when Fourier-transformed, to a function of three variables, as  $H(z_1, z_2; q)$ . We have determined  $H$  for interfaces[22] and also for coarse-grained (CG) bilayers[23]. Then, as it must,  $H$  reproduces  $S$  in a computation of

$$\int_0^L dz_1 \int_0^L dz_2 (z_1 - z_0) H(z_1, z_2; q) (z_2 - z_0).$$

The method by which these well founded results are obtained uses the positions of heads of amphiphilic molecules,  $x_j, y_j, z_j$  and interprets  $z_j$  as the local "height"  $h(x_j, y_j)$  so that

$$\tilde{h}(\mathbf{q}) = \text{const.} \sum_j z_j \exp[i\mathbf{q}\mathbf{R}_j].$$

The preselected set of values of  $\mathbf{q} = (q_x, q_y)$  must follow the usual rules, but the above sums are approximations (in the spirit of the Monte-Carlo integration) because the theory of Fourier series defines the coefficients such as  $\tilde{h}$  as *integrals* over the function  $h(x, y)$ .

However, and that is the final point of this Letter, there exists a known modification of this last method, due to the Max-Planck(Potsdam) laboratory[24,25], little used[23-25], which answers the following question: " given a set of points  $(z_j, x_j, y_j)$  what is the best surface  $h(x, y)$  represented by a finite Fourier series?". The obvious "best" and most natural one is "best in the least-squares sense". Such  $h(x, y)$  minimizes the sum of squares of the deviations  $h(x_j, y_j) - z_j$ . The problem so posed is solved as a standard linear problem and the resulting finite Fourier series have been computed[23-25]. That is done for each snapshot (each "time" in the simulation run) and the resulting power spectra are then averaged over the entire simulation run. As  $q_x = (2\pi/L_x)n_x$  and similarly  $q_y$ , we deal with  $n_x, n_y$ . Once a maximum value of  $n_y$  is assumed it defines a rectangle (half of a square) and the set of resulting  $q$ -vectors is used. The size of the matrix in the linear problem is 81 for  $n_{max} = 4$ , 625 for 12, 1369 for 18,... . The limit is set by the number of data points, which reasonably ought to be no smaller than twice the number of coefficients, or larger.

There can be no simpler nor more direct implementation of the "best" Fourier series  $h(x, y)$  to represent the simulation data. And it supports the "sum-over-points" method, not the gridding method. The tests, applying the "sum-over-points" method and the "least-squares method" to the same collection of positions of heads - demonstrate that these two methods of obtaining the power spectrum agree as well as one can expect or hope.

Figure 1 shows such an example from one long run at an almost tensionless state with  $S$  produced by the "sum-over-points method", and three plots of  $S$  by the least-squares method. Clearly the agreement of shapes is excellent and all show a nearest-neighbor peak or, if the range of  $q$  is too small, a minimum in  $S(x)$ .

It may be noted as an aside that the low-q divergence does not change visibly with the decrease of  $n_{max}$  even down to value of 4.

These tests demonstrate that the "sum-over-points method" produces correct and reliable results.

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## Figure Captions.

Caption to Fig.1

Comparison of  $S(q)$  (by the direct-sum method) with that obtained by the least-squares method (see text) for 81, 625, and 441 Fourier coefficients. The identity of shapes demonstrates the reliable accuracy of the "direct-sum-over-heads" method of calculating  $\tilde{h}(\mathbf{q})$ . A simplified CG model[26-28] of bilayer at  $kT/\epsilon = 1.1$ , overall density  $\rho = 0.892$ , monolayer with  $N_1 \sim 2000$  amphiphiles, box edge  $L_x = 38.25$ , 5=4+1 beads and Lennard-Jones solvent.

## Supplementary Material.

The Taylor series for  $x^2S$  leads to a Laurent series for  $S$ , introduced in the main text as

$$S = a_{-2}/x^2 + a_{-1}/x + a_0 + a_1x + a_2x^2 + \dots$$

with  $x \equiv |q^2|$ . It is of some interest to show that a polynomial obtained by cutting the series at e.g.  $a_4x^4$ , is capable of reproducing reasonably well the data points of  $S(q)$  in the extensive range of  $0 < q < 2\pi/\sigma$ . Here  $\sigma$  is the collision diameter, common to all particles and beads in the Coarse Grained model used.

Figure 1S shows raw data for a tensionless state of such a coarse-grained model(CG) of a bilayer; the deviations from the fit of the Laurent series cut at  $a_4$  are shown as vertical bars (impulses). Even without further refining of this polynomial fit, the example shows that such representation is feasible. The same raw data obtained by the direct "sum-over-heads" method are compared in the main text with the obviously valid method based on least-squares approximation and introduced by the Max-Planck (Potsdam) laboratory.

### Supplementary Material. Figure 1S

Caption to Fig.1S

The Figure 1S shows the so-called structure factor i.e fluctuation spectrum  $S = \langle \tilde{h}\tilde{h}^* \rangle$  in the range about  $q \in (0, 2\pi/\sigma)$ , plotted against  $x = q^2$  and showing (1) the divergence; (2) the minimum; (3) the nearest-neighbor peak. Deviations from a simple fit to Laurent series with 7 terms, are shown with vertical lines (impulses). A simplified CG model of bilayer at  $kT/\epsilon = 1.1$ , overall density  $\rho = 0.892$ , monolayer with  $N_1 \sim 2000$  amphiphiles, box edge  $L_x = 38.25$ , area  $L_x^2$ , 6.E6 timesteps, 5=4+1 beads and Lennard-Jones solvent.

Fig.1

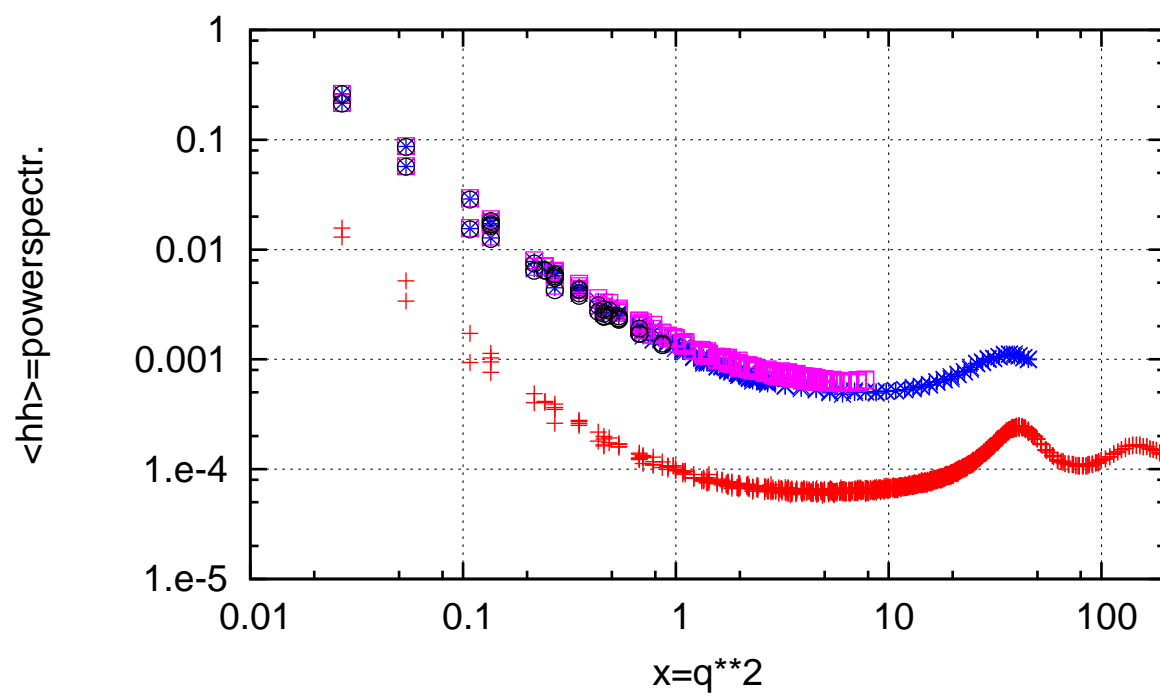




Fig.1S

